

Evaluation of 2.25Cr-1Mo Alloy for Containment of LiCl/KCl Eutectic During the Pyrometallurgical Processing of Used Nuclear Fuel

TMS 2011 Annual Meeting

B. R. Westphal
S. X. Li
G. L. Fredrickson
D. Vaden
T. A. Johnson
J. C. Wass

March 2011

This is a preprint of a paper intended for publication in a journal or proceedings. Since changes may be made before publication, this preprint should not be cited or reproduced without permission of the author. This document was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, or any of their employees, makes any warranty, expressed or implied, or assumes any legal liability or responsibility for any third party's use, or the results of such use, of any information, apparatus, product or process disclosed in this report, or represents that its use by such third party would not infringe privately owned rights. The views expressed in this paper are not necessarily those of the United States Government or the sponsoring agency.

The INL is a
U.S. Department of Energy
National Laboratory
operated by
Battelle Energy Alliance



EVALUATION OF 2.25Cr-1Mo ALLOY FOR CONTAINMENT OF LiCl/KCl EUTECTIC DURING THE PYROMETALLURGICAL PROCESSING OF USED NUCLEAR FUEL

B.R. Westphal, S.X. Li, G.L. Fredrickson, D. Vaden, T.A. Johnson, and J.C. Wass

Idaho National Laboratory; P.O. Box 1625; Idaho Falls, ID 83415, USA

Keywords: Pyroprocessing, Molten Salt, Corrosion

Abstract

Recovery of uranium from the Mk-IV and Mk-V electrorefiner vessels containing a LiCl/KCl eutectic salt has been on-going during the pyrometallurgical processing of used nuclear fuel for 14 and 12 years, respectively. Although austenitic stainless steels are typically utilized for LiCl/KCl salt systems, the presence of cadmium in the Mk-IV electrorefiner dictates an alternate material. A 2.25Cr-1Mo alloy (ASME SA-387) was chosen due to the absence of nickel in the alloy which has a considerable solubility in cadmium. Using the transition metal impurities (iron, chromium, nickel, molybdenum, and manganese) in the electrorefined uranium products, an algorithm was developed to derive values for the contribution of the transition metals from the various input sources. Weight loss and corrosion rate data for the Mk-V electrorefiner vessel were then generated based on the transition metal impurities in the uranium products. To date, the corrosion rate of the 2.25Cr-1Mo alloy in LiCl/KCl eutectic is “outstanding” assuming uniform (i.e. non-localized) conditions.

Introduction

Low-enriched uranium products are being recovered from the Experimental Breeder Reactor-II (EBR-II) and Fast Flux Test Facility (FFTF) used nuclear fuels by a pyrometallurgical treatment process at the Idaho National Laboratory (INL). The treatment process comprises a set of operations designed to neutralize bond sodium, recover uranium from radioactive fission products, and place the fission products into acceptable waste forms [1-2]. Reactive sodium metal, essential for heat transfer purposes during reactor operations, is readily converted to chloride during the process. Electrorefined uranium products are currently being stored pending a final disposition decision. Treatment of the EBR-II used driver fuel was initiated in June 1996 while blanket fuel processing started in September 1998. These treatment processes continue on the balance of the used fuels.

Batch operations performed on the used fuel in the Fuel Conditioning Facility (FCF) include chopping, electrorefining, cathode processing, and casting. The FCF maintains two hot cells, an air cell and an argon cell, which are both atmosphere-controlled and shielded. All operations within the cells are performed remotely by overhead cranes, electromechanical manipulators, or manual manipulators. Used fuel is either dismantled into elements from assemblies or retrieved directly as elements from storage containers. Initial fuel element handling operations are performed in the air cell of FCF prior to being transferred to the argon cell for element chopping. Argon cell impurities, such as oxygen and water vapor, are kept at levels below approximately 100 ppm to minimize contamination concerns. The elements are chopped into segments by a solenoid-driven press for both driver and blanket fuel types. Driver fuel was utilized in the core

region of the reactor and contains a highly enriched uranium-zirconium alloy. Blanket fuel, consisting of depleted uranium, encircled the driver-core. Both fuel types are clad with austenitic-based stainless steels (304SS, 316SS, and D9).

The segments are then loaded into a stainless steel (304SS) anode assembly which contains up to nine perforated baskets depending on the fuel type. The anode assembly is installed into the electrorefiner commensurate with the fuel type; Mk-IV for driver fuel and Mk-V for blanket fuel. The two electrorefiner vessels are identical in design but differ in the electrode configurations, liquid contents, and process conditions. During electrorefining [3], fuel is anodically dissolved in a molten (500°C) LiCl-KCl eutectic salt such that the transport and deposition of uranium on a cathode is feasible. In addition to the LiCl-KCl, other chloride species accumulate in the electrorefiner salt due to the oxidation of fission products, bond sodium, and actinides present in the used fuel. The electrorefined uranium is deposited on a steel cathode and harvested for subsequent processing in a vacuum distillation furnace. The cathodes consist primarily of uranium with some adhering chloride salts. Distillation operations for the removal of the salt from the cathode products are performed in a single cathode processor to produce consolidated metal ingots. A casting step following distillation allows for isotopic dilution, if necessary, and sampling of the uranium ingots for chemical analyses.

A very thorough description of the design, operation, and criticality concerns for the Mk-IV and Mk-V electrorefiners are given elsewhere [4-5]. Selection of the electrorefiner vessel material was based on the presence of cadmium in the Mk-IV electrorefiner. The purpose of the cadmium pool in the Mk-IV electrorefiner is for the recovery of cathodic uranium dendrites that fall off or are dislodged by the cathode scrapers. The Mk-V electrorefiner does not have a cadmium pool due to a different anode to cathode arrangement; a module which contains both the anode and cathode. Without cadmium, the selection of a material for the containment of LiCl-KCl salt would have been either a mild steel or an austenitic stainless steel (304SS or 316SS) based on corrosion studies [6-9]. Since the cadmium has a high solubility for nickel [10], the austenitic steels were eliminated and a 2.25Cr-1Mo alloy (ASME SA387) was chosen for the Mk-IV electrorefiner vessel. The Mk-V electrorefiner vessel is also 2.25Cr-1Mo alloy based on the Mk-IV selection.

The scope of this paper is to evaluate the performance of the 2.25Cr-1Mo alloy electrorefiner vessel via the transition metal impurities (iron, chromium, nickel, molybdenum, and manganese) in the uranium products. A description of the sources of transition metal impurities is provided followed by their concentrations in the uranium products. From the impurity concentrations, an algorithm was developed to determine the contribution of the electrorefiner vessel to the impurities. Corrosion data is then presented for the 2.25Cr-1Mo alloy Mk-V electrorefiner vessel.

Experimental

The transition metals of interest for this evaluation are iron, chromium, nickel, molybdenum, and manganese due to their detection in significant quantities (1-1000 ppm) following the chemical analyses of electrorefined uranium products. Following the ingot casting step, cast pin samples are dissolved in nitric acid and analyzed by inductively coupled plasma optical emission spectroscopy (ICP-OES) for several analytes including the transition metals of interest. Typical quantities of transition metals detected by ICP-OES range from zero to 1000 ppm and measurement errors are on the order of \pm 5-10 wt. % of the reported concentrations.

For this study, the Mk-V electrorefiner system was chosen for evaluation due to the absence of the cadmium pool, a fuel clad material (304SS) that matches the anode-cathode module (ACM), and data on the composition of the unirradiated or cold blanket fuel [11]. Since cadmium has some solubility for the transition metals [10], it could be an additional source of transition metals if included in this study. Thus, shown in Table I are the four primary sources of transition metals during processing of used blanket fuel, all of which focus on the electrorefining operation. Although other sources are conceivable, such as auxiliary process and in-cell handling equipment, they are considered negligible in their contribution as impurities to the uranium products. Iron, nickel, and manganese were detected as impurities in the cold fuel [11]. Molybdenum is the only in-reactor transition metal generated in significant quantities as a fission product and is also listed in the blanket fuel column. The blanket fuel clad and anode-cathode module include all the transition metals of interest. The 2.25Cr-1Mo alloy electrorefiner vessel has a manganese concentration of approximately 0.5 wt. %.

Table I. Primary Sources of Transition Metals during Processing of Blanket Fuel

| Transition Metal | Blanket Fuel | Fuel Clad | Anode-Cathode Module | Electrorefiner Vessel |
|------------------|--------------|-----------|----------------------|-----------------------|
| Fe | X | X | X | X |
| Cr | | X | X | X |
| Ni | X | X | X | |
| Mo | X | X | X | X |
| Mn | X | X | X | X |

Results

Following the chemical analyses for the transition metal impurities in the cast pin samples of the electrorefined blanket uranium products, the data from fifteen batches were averaged and are shown in Table II along with the standard deviations in brackets. The batches were chosen based on their typical operating conditions at the Mk-V electrorefiner and the detection of all the transition metal impurities. Averaging the data alleviates the batch to batch fluctuations caused by test variations and analytical errors and allows for consistency in the data. Iron is the largest impurity contributor to the uranium products followed by molybdenum, manganese, chromium, and nickel.

Also shown in Table II is the contribution of transition metal impurities from the aforementioned sources. The ACM and fuel clad sources have been combined since both consist of 304SS. A set of twelve linear equations was solved for twelve unknowns to derive the values shown in Table II. The relative compositions of the transition metals in 304SS and 2.25Cr-1Mo alloy were used in the algorithm as well as dissolution factors based on the electromotive force series data [12]. For example, the selective diffusion of chromium and the relative corrosion rates of iron to nickel in a LiCl-KCl system have been noted [8, 13]. The dissolution factors are only a first approximation with no regard to the activity coefficients and interaction parameters of the system.

Since the transition metals in the uranium products have been averaged, their contribution from the sources also represents averaged values. Iron is fairly distributed across the three sources in

Table II with the 304SS components (ACM and clad) contributing the highest amount. Most of the chromium in the uranium products is attributed to the 304SS sources. The primary source of nickel is as an impurity from the blanket fuel and the secondary source is the 304SS. As mentioned, molybdenum is a fission product and contributes significantly to the uranium product impurities. Manganese in the blanket fuel and from the vessel account for the majority of the manganese in the uranium products.

Table II. Transition Metal Impurities in Blanket Uranium Products and their Sources

| Transition Metal | Uranium Products (ppm) | Blanket Fuel (ppm) | ACM & Clad (ppm) | Electrorefiner Vessel (ppm) |
|------------------|------------------------|--------------------|------------------|-----------------------------|
| Fe | 453 [117] | 119 | 179 | 154 |
| Cr | 75 [28] | - | 70 | 5 |
| Ni | 66 [17] | 41 | 25 | - |
| Mo | 110 [16] | 108 | 2 | 1 |
| Mn | 76 [13] | 48 | 2 | 26 |

The amount of molybdenum attributed to the blanket fuel as fission product can be compared against previous data for another similar noble metal (Ru^{106}) fission product [14]. Assuming the concentration of molybdenum in typical irradiated blanket fuel is 140 ppm, 77% of the molybdenum is applied to the blanket fuel by the algorithm. This compares favorably to the 80% value for Ru^{106} reported previously.

The individual masses of the transition metals in the Mk-V electrorefiner vessel, based on known dimensional and compositional data, are shown in Table III. In the third and fourth columns are the calculated amounts of transition metals lost from the vessel as impurities and weight loss values of the vessel, respectively. Although the overall weight loss of the vessel is less than 0.2%, the amount of manganese lost is much higher. Possible explanations are another source of manganese not considered in this analysis or preferential corrosion of manganese relative to the other transition metals due to dissolution kinetics and/or oxidation potentials. A test has been performed in the Mk-V electrorefiner without a uranium-loaded anode wherein uranium was transported from the vessel walls to a set of cylindrical cathode rods. The uranium collects on the walls during standard electrorefining operations in the Mk-V. The uranium product collected on the rods was rich in manganese (46 ppm) relative to iron (97 ppm) and chromium (17 ppm) leading to the conclusion that manganese may be transferred from the vessel in disproportionate amounts. Thus, it would appear that manganese is reacting preferentially although more testing is needed to establish consistency in the data.

Using the total mass of transition metals found in the uranium products from the Mk-V electrorefiner vessel, a corrosion rate was calculated based on the assumption of uniform thinning. A rate of 0.06 mils/year (mpy) is derived which is lower than previous iron-based systems [7]. Rated on a relative corrosion scale [15], any value less than 1 mpy is considered “outstanding” or the highest rating. Corrosion coupons have also been placed in both electrorefiner salt regions and results to date indicate negligible signs of corrosion. Surveillance of the corrosion coupons will continue in order to assess the performance of the electrorefiner vessels.

Table III. Mk-V Electrorefiner Vessel Weight Loss for Individual Transition Metals

| Transition Metal | Mk-V Electrorefiner Vessel (g) | Impurity in Uranium Products from Vessel (g) | Vessel Weight Loss (%) |
|------------------|--------------------------------|--|------------------------|
| Fe | 333,854 | 502 | 0.15% |
| Cr | 7,855 | 15 | 0.19% |
| Mo | 3,491 | 3 | 0.07% |
| Mn | 1,571 | 84 | 5.34% |
| Total | 346,771 | 603 | 0.17% |

Conclusions

Transition metal impurities detected in the uranium products following the treatment of used EBR-II blanket fuel were assigned to three primary sources; blanket fuel, 304SS anode-cathode/clad, and the electrorefiner vessel. For the electrorefiner vessel, iron, chromium, molybdenum, and manganese quantities were adjusted for their loss to the uranium products. While iron, chromium, and molybdenum losses are comparable, the manganese value is significantly greater, due most likely to preferential reaction from the 2.25Cr-1Mo alloy. The overall corrosion rate of the Mk-V electrorefiner vessel is rated as “outstanding” but the loss of manganese is a concern and will be continuously monitored.

Acknowledgements

The authors would like to acknowledge the Fuel Conditioning Facility operations personnel for their contributions and the Analytical Laboratory organization for chemical services. Work supported by the U.S. Department of Energy, Office of Nuclear Energy, Science, and Technology, under DOE-NE Idaho Operations Office Contract DE-AC07-05ID14517.

References

1. Y.I. Chang, “The Integral Fast Reactor,” *Nucl. Tech.*, 88 (1990).
2. B.R. Westphal and R.D. Mariani, “Uranium Processing during the Treatment of Sodium-Bonded Spent Nuclear Fuel,” *JOM*, 52 (9) (2000), 21-25.
3. S.X. Li and M.F. Simpson, “Anodic Process of Electrorefining Spent Driver Fuel in Molten LiCl-KCl-UCl₃/Cd System,” *Min. Met. Proc.*, 22 (4) (2005).
4. J.E. Herceg et al., “Engineering and Acquisition of Equipment for Electrometallurgical Treatment of Spent Nuclear Fuel,” *Proc. ICONE 8* (Baltimore, MD: ASME, 2000).
5. R.D. Mariani et al., “Criticality Safety Strategy and Analysis Summary for the Fuel Cycle Facility Electrorefiner Argonne National Laboratory West,” *Nucl. Tech.*, 114 (1996), 224-34.
6. F. Colom and A. Bodalo, “Corrosion of Iron (Armco) in KCl-LiCl Melts,” *Corr. Sci.*, 12 (1972), 731-38.
7. J.E. Battles et al., “Materials Corrosion Molten-Salt Lithium/Sulfur Cells,” *Corrosion Problems in Energy Conversion and Generation*, ed. C.S. Tedmon, Jr. (Princeton, NJ: The Electrochemical Society, 1974), 20-31.
8. A.R. Shankar and U.K. Mudali, “Corrosion of Type 316L Stainless Steel in Molten LiCl-KCl Salt,” *Mat. and Corr.*, 59, 11 (2008), 878-82.

9. C.S. Wang et al., "Study on the Corrosion Behavior of 316L Stainless Steel Immersed in Molten LiCl-KCl," *Proc. Global 2009* (Paris, France: ANS, 2009), 1325-30.
10. M.G. Chasanov et al., "Solubility of 3-d Transition Metals in Liquid Cadmium," *Trans. Met. Soc. AIME*, 224 (1962), 935-8.
11. L.C. Walters et al., "Performance of Metallic Fuels and Blankets in Liquid-Metal Fast Breeder Reactor," *Nucl. Tech.*, 65 (1984), 179-230.
12. J.A. Plambeck, "Volume X: Fused Salt Systems," *Encyclopedia of Electrochemistry of the Elements*, ed. A.J. Bard (New York, NY: Marcel Dekker, 1976), 68-71.
13. X.K. Feng and C.A. Melendres, "Anodic Corrosion and Passivation Behavior of Some Metals in Molten LiCl-KCl Containing Oxide Ions," *J. Electrochem. Soc.*, 129 (6) (1982), 1245-49.
14. B.R. Westphal et al., "Fate of Noble Metals during the Pyroprocessing of Spent Nuclear Fuel," *Proc. Global 2009* (Paris, France: SFEN, 2009).
15. M.G. Fontana, *Corrosion Engineering* (New York, NY: McGraw-Hill Book Co., 1986), 172.